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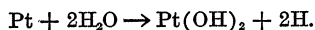
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THE RELATION BETWEEN PHOTOSYNTHESIS OF  
CARBON DIOXIDE AND NITRATE REDUCTION

THE first step in the utilization of nitrates for protein synthesis by the plant leaf is no doubt a reduction of the nitrate to the nitrite and finally to ammonia. The rôle played by sunlight in this action has been investigated from several sides. While Schimper tried to demonstrate that it was by means of light only, and in the cell containing chlorophyll, that nitrate reduction takes place, this theory has been somewhat modified by the researches of Zaleski, of Suzuki and especially of Godlewski to the effect that while nitrate reduction and concomitant protein synthesis take place to a much greater extent in the light, these reactions do also take place in the dark.

The writer has found that perfectly sterile aqueous solutions of potassium or calcium nitrate will keep in the dark, even at 95°, indefinitely without forming a trace of nitrite. If, however, a small quantity of colloidal platinum is added, a reduction of the nitrate soon sets in with the formation of nitrites and of ammonia, as made very evident with the Gries's and Nessler's reagent, respectively. This observation is quite in harmony with that of Schoenbein, who noticed a reduction of nitrates by means of juices of certain fungi, *confervæ*, etc. As most of the common forms of bacteria possess the property, to some extent at least, of reducing nitrates, it is of course very important to exclude all bacteria from the mixture.

That this reaction is brought about by means of hydrogen peroxide I am very much inclined to doubt, for absolutely no reduction takes place in the presence of hydrogen peroxide, with or without colloidal platinum; nor is the reaction in the least inhibited in vacuo. More probable does it appear that the platinum acts as follows, if there is something present to take up the hydrogen formed:<sup>1</sup>



The hydrogen is kept in the active, or nascent, state by the platinum, and reduces the ni-

trate directly. The platinum hydroxide in turn splits into platinum and hydrogen peroxide; the latter decomposes to water with the liberation of oxygen:



The increased reduction of nitrates and of protein synthesis in the leaf in the light can be understood from the following observations. It was found that the reduction of potassium and calcium nitrates takes place with remarkable ease in the ultra-violet light of the quartz mercury vapor lamp, forming nitrite, ammonia and oxygen. The same action takes place, though more slowly, in the sunlight and even in diffuse or sky light. The action is greatly accelerated by colloidal platinum, though the latter is not necessary. Of special importance is the fact that the reduction of these nitrates results in a decidedly *alkaline* solution.

The theory that formaldehyde is the first product of reduction in the carbon dioxide appropriation has, of late, gained much substantiation. It must be remembered, however, that the next step, the polymerization of formaldehyde to carbohydrates takes place in alkaline solution only. Now while of course it is true that nitrate reduction in the leaf takes place in the dark, it can not be denied that this action is much greater in the light, and, as Schimper has shown, in the neighborhood of the chloroplasts; which must then result in a local alkalinity at these points. Thus not only are the proper conditions for carbohydrate synthesis established, but nitrogen is also produced in the best form and at the most available place for protein synthesis. No other explanation has been given so far as my information goes, and I can conceive no other way in which these very necessary conditions can be produced in the midst, it might be said, of all the acid products of sugar and protein metabolism. In this connection mention might also be made of a micro-chemical observation of MacCallum<sup>2</sup> who found potassium localized in the immediate neighborhood of the chloroplasts.

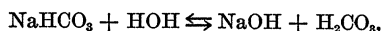
<sup>1</sup> See Mond and Ramsay, *Zeit. f. phys.-chem.*, **25**, 657. Bredig and von Berneck, *ibid.*, **31**, 254.

<sup>2</sup> *Jour. of Phys.*, **32**, 95, 1905.

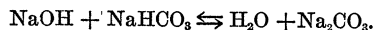
But an alkaline area in connection with the chlorophyll can be of even greater importance. It is, in fact, highly probable that the reduction of carbon dioxide itself takes place in an alkaline solution, or better in the form of a bicarbonate. It will be remembered that while in the various attempts of Lieben,<sup>3</sup> Ballo<sup>4</sup> and of Fenton,<sup>5</sup> to reduce carbonic acid by chemical means, formic acid only was produced, the reaction took place either only with the alkaline bicarbonate or it was greatly accelerated by the presence of alkali.

While the experiments of Herchenfinkle,<sup>6</sup> and of Berthelot and Gaudechon<sup>7</sup> on the decomposition of carbon dioxide into carbon monoxide and oxygen in ultra-violet light are a valuable contribution to the chemistry of carbon dioxide, It must be borne in mind that in the plant leaf we are dealing with a substance of very different properties, namely, metacarbonic acid or its salts.

That certain plants are capable of liberating oxygen and synthesizing carbohydrates from solutions of alkaline bicarbonates has been demonstrated by Draper, Hassak, Nathanson, Anglestein<sup>8</sup> and others. These results can not be interpreted to mean that the plant is capable of utilizing the alkaline bicarbonates directly, but as the liberation of oxygen decreases with increasing alkalinity, it is clear from the equation,



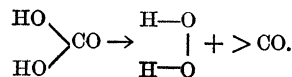
that the plant is utilizing the  $\text{H}_2\text{CO}_3$  formed by hydrolysis of the sodium bicarbonate. As McCoy<sup>9</sup> has shown, the amount of sodium hydroxide present in the above reaction is decreased to about one twentieth of the amount calculated for a normal hydrolysis, because of the secondary reaction:



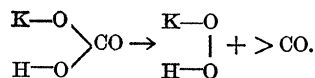
Thus it is clear that the plant has consider-

able carbonic acid at its disposal, which it can utilize until the solution becomes too strongly alkaline. It must be noted that from the beginning, the action is taking place in an alkaline medium. Of special importance in this connection are the observations of Klebs<sup>10</sup> and of Hassak<sup>11</sup> who found that various forms of algæ growing in distilled water produce alkalinity therein during active appropriation of carbon dioxide in the sunlight.

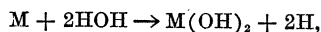
In view of these facts, how then can the reduction of carbonic acid be pictured? Nef<sup>12</sup> has suggested that the first step in photosynthesis is as follows:



Now it is highly probable that the degree of dissociation brought about by light is greatly increased in the case of the alkaline bicarbonate:



This decomposition is, of course, similar to the decomposition of carbon dioxide into carbon monoxide and oxygen by means of ultra-violet light studied by Herchenfinkle. The potassium hydrogen peroxide decomposes, reforming potassium hydroxide, and liberating oxygen. The  $\text{OC}<$  is immediately reduced to formaldehyde by an action analogous to the catalytic reduction of the nitrates as given above:



The detailed steps in the argument have not been fully developed in the above brief notice. Further work along these lines, as well as on the relation between plant acids and protein synthesis, are in progress, and will be published fully elsewhere.

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<sup>3</sup> *Monatsh. f. Chem.*, 1895 and 1897.

<sup>4</sup> *Berl. Ber.*, 1884, 6.

<sup>5</sup> *Jour. Chem. Soc. London*, 91, 689.

<sup>6</sup> *Compt. rend.*, 149, 395.

<sup>7</sup> *Ibid.*, 151.

<sup>8</sup> Dissertation, Halle, 1910.

<sup>9</sup> *Amer. Chem. Jour.*, 29, 437.

<sup>10</sup> *Unters. Bot. Inst. Tuebingen*, 2, 340.

<sup>11</sup> *Ibid.*, 465.

<sup>12</sup> *Ann. Chem. (Liebig)*, 357, 253.